MOLECULAR SIMULATION STUDIES OF MDEA ABSORPTION PROCESS FOR CO_2 CAPTURE

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ABSTRACT

Concentration of CO_2 in the earth is gradually increasing every year due to the increased energy use by an expanding economy and population, and an overall growth in emissions come from electricity generation and transportation. Since CO_2 is a greenhouse gas, it will trap the heat inside the earth from reflecting back to the outer space and consequently contribute to global warming. So, methyldiethanolamine (MDEA) absorption for CO_2 capture process is developed to combat this trend due to its relatively high capacity, a low vapor pressure and small enthalpy of reaction with acid gases. Therefore, a research of studying methyldiethanolamine (MDEA) absorption process for CO_2 capture through simulation is developed so that the intermolecular interaction between the solvent (MDEA) and the acid gas (CO_2) during the absorption process can be investigated. Through the simulation, the optimum temperature of the carbon dioxide absorption will be determined. Molecular dynamic (MD) simulation will be used to study the interaction of molecule and give an insight on CO_2 absorption process. To perform the molecular dynamic (MD) simulation two boxes of carbon dioxide gas and MDEA solvent will combine to study the absorption process. Moreover, thermodynamic condition under NVE, NPT and NVT will be set and the simulation results will be interpreted in terms of radical distribution function. Mean square displacement (MSD) is then used to determine the diffusivity of molecules. MD simulation is performed at temperature of 40°C and 45°C to observe the potential interaction of molecules. Binary system studies the solubility of MDEA in water. Tertiary system studies the potential interaction of CO_2 in MDEA solution. It can be concluded that the molecular dynamic simulation clearly shows the potential interaction of molecules and its behaviour.

ABSTRAK

Kepekatan CO_2 di bumi meningkat secara beransur-ansur setiap tahun disebabkan peningkatan penggunaan tenaga oleh ekonomi dan penduduk yang berkembang, dan pertumbuhan keseluruhan dalam pengeluaran daripada penjanaan elektrik dan pengangkutan. Oleh sebab CO_2 ialah gas rumah hijau, ia akan memerangkap haba yang di dalam bumi daripada dicerminkan kembali ke angkasa lepas dan seterusnya menyumbang kepada pemanasan global. Jadi, proses penyerapan melalui methyldiethanolamine (MDEA) untuk menangkap CO_2 melalui simulasi dibangunkan untuk memerangi trend ini disebabkan kapasiti yang agak tinggi, tekanan wap yang rendah dan entalpi tindak balas dengan gas asid yang kecil. Oleh itu, satu penyelidikan tentang proses penyerapan melalui methyldiethanolamine (MDEA) untuk menangkap CO_2 melalui simulasi dibangunkan supaya interaksi antara molekul antara pelarut (MDEA) dan gas asid (CO_2) semasa proses penyerapan boleh difahami. Melalui simulasi, suhu optimum bagi penyerapan karbon dioksida akan ditentukan. Simulasi dinamik molekul (MD) akan digunakan untuk mengkaji interaksi antara molekul dan memberi gambaran mengenai proses penyerapan CO_2. Untuk melaksanakan simulasi dinamik molekul (MD) dua kotak gas karbon dioksida dan pelarut MDEA akan bergabung untuk mengkaji proses penyerapan. Selain itu, keadaan termodinamik di bawah NVE, NPT dan NVT akan ditetapkan dan keputusan simulasi akan ditafsirkan dari segi fungsi taburan yang radikal. Mean square displacement (MSD) kemudiannya digunakan untuk menentukan kemeresapan molekul. Simulasi MD dilakukan pada suhu 40°C dan 45°C untuk memerhati interaksi potensi molekul. Sistem binari mengkaji keterlarutan MDEA dalam air. Sistem ketiga mengkaji interaksi potensi CO_2 dalam MDEA. Ia boleh disimpulkan bahawa simulasi dinamik molekul jelas menunjukkan interaksi potensi molekul dan kelakuannya.

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LIST OF ABBREVIATIONS

a_i	Acceleration
ε_o	Vacuum permittivity
ε_T	Relative permittivity
f_i	Force of Newton's second law of motion
m_i	Mass of particle
ρ	Density of atoms
r	Spherical radius
r_i	Change in particle position
$V(r_i)$	Potential energy respect to particle position
t	Time
∇_i	3 dimensions
Φ	Harmonic interaction force
Ψ_{nlm_l}	Wave function

Greek

Å	Angstrom
E	Energy
K	Harmonic force constant
M	Diffusion coefficient
N	Number of mole
N_i	atomic population
P	Pressure
P_{ii}	density matrix
S_{ii}	overlap matrix
T	Temperature
U_{AB}	Potential Energy
V	Volume

LIST OF ABBREVIATIONS

AO	Atomic orbitals
COMPASS	Condensed-phase optimized molecular potentials for atomic simulation studies
DEA	Diethanolamine
LJ	Lennard-Jones potential
LPA	Löwdin population analysis
MEA	Monoethanolamine
MD	Molecular dynamics simulation
MDEA	Methyldiethanolamine
MM	Molecular mechanic
MO	Molecular wave functions
MPA	Mulliken population analysis
MSD	Mean square displacement
NPT	Constant number of moles, pressures and temperatures
NVE	Constant number of moles, volumes and energies
NVT	Constant number of moles, volumes and temperatures
PBC	Periodic boundary condition (PBC)
QM	Quantum mechanic
RDF	radial distribution function

1 INTRODUCTION

1.1 Motivation and statement of problem

Nowadays, the issue of CO_2 emissions becomes more serious due to the increased energy use by an expanding economy and population, and an overall growth in emissions from electricity generation and transportation. All these human activities are altering the carbon cycle by adding more CO_2 to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO_2 from the atmosphere. This phenomenon causes the trapping of CO_2 inside the earth to increase drastically for past few decades (Rubin & De Coninck, 2005).

The CO_2 emissions bring bad effect to human beings and also environment too. Global warming caused by the trapping of CO_2 in the earth melts the ice caps from north and south poles corresponding to the rise of sea level. Densely settled coastal plains would become uninhabitable with just a small rise in sea level. Warming would result in the increased of high cloud cover in winter, giving chemical reactions a platform in the atmosphere, which could result in depletion of the ozone layer. A warmer climate could change the weather systems of the earth, meaning there would be more droughts and floods, and more frequent and stronger storms. Diseases would be able to spread to areas which were previously too cold for them to survive in. As with the diseases, the range of plants and animals would change, with the net effect of most organisms moving towards the North and South Poles.

Figure 1-1 shows that a large quantity of CO_2 is released every year due the combustion of fossil fuel to produce energy. The CO_2 emissions from fossil fuel combustion are increasing drastically especially from year 1990 to 2010. There are a few of carbon dioxide separation technologies but the chemical absorption is the most effective for the removal of carbon dioxide. In this study, the chemical solution used for process of chemical absorption is amine solution. The reaction between CO_2 and amines will enhance the driving force for the separation even at low partial pressure of CO_2 (IEA org, 2013).

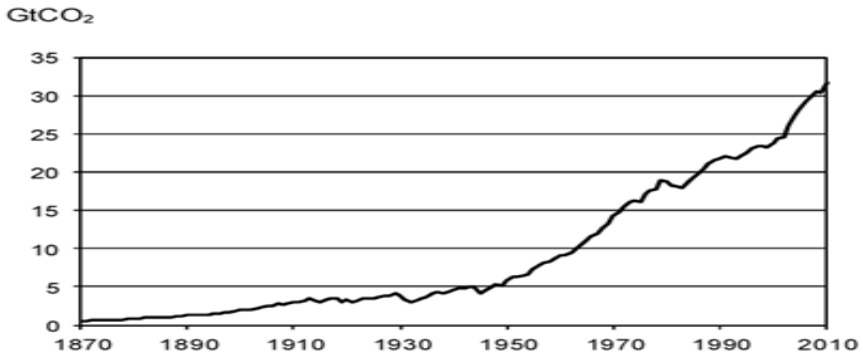

Figure 1-1: Trend in CO_2 emissions from fossil fuel combustion (IEA org, 2013)

Figure 1-2 shows that electricity and heat emits the highest total amount of CO_2 to the atmosphere compared to other sectors. Generation of electricity and heat worldwide relies heavily on coal, the most carbon-intensive fossil fuel. Countries such as Australia, China, India, Poland and South Africa produce over two-thirds of their electricity and heat through the combustion of coal. By 2035, the WEO 2013 projects that demand for electricity will be almost 70% higher than current demand, driven by rapid growth in population and income in developing countries, by the continuing increase in the number of electrical devices used in homes and commercial buildings, and by the growth in electrically driven industrial processes (IEA org, 2013).

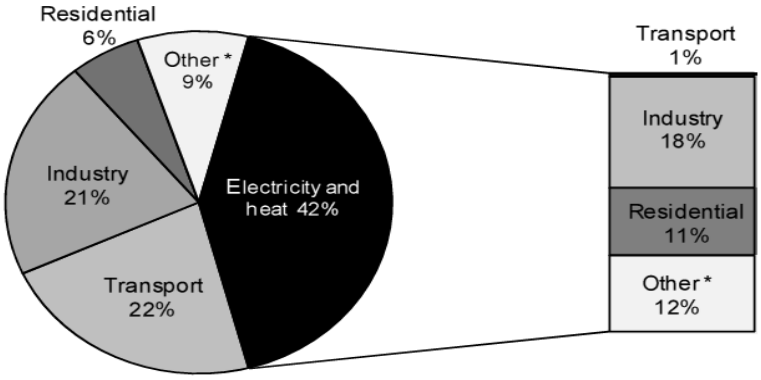

Figure 1-2: World CO_2 emissions by sector in 2011 (IEA org, 2013)

Therefore, the aim of this study is to understand the molecular level interaction during the process of CO_2 absorption using amine solution. The molecular dynamic simulation is used to simulate the molecular interaction of the absorption process. Through this simulation, the molecular interaction between amine solution and CO_2 can be understood better and can be applied to improve the performance of amine absorption

process. The outcome from this study can be used for future research on CO_2 capture to conserve and preserve our natural environment.

1.2 Objectives

This research project aims to:

- Study intermolecular interaction in methyldiethanolamine (MDEA) absorption for carbon dioxide capture via molecular dynamic simulation technique at different process operating conditions. The strength of intermolecular interaction between the CO_2 and the solvent will represent the absorption effectiveness.

1.3 Scope of this research

In this case study there are few scopes:

- Molecular Dynamic (MD) simulation is used to study and give insight on the intermolecular interaction between solvent and acid gases in the absorption process.
- There are different systems at various operating conditions are considered in this study; pure molecules (pure MDEA, pure water, and pure CO_2), binary system (MDEA+H_2O) and tertiary system (MDEA+CO_2+H_2O).
- The optimum molecular interaction will be determined by observing the highest intermolecular interaction between molecular while simulating the absorption process at different temperature.
- Mean square displacement is used to calculate the diffusion coefficient.

1.4 Main contribution of this work

This study gives insight on the molecular interaction between carbon dioxide and methyldiethanolamine (MDEA) during the absorption process. The maximum interaction during the absorption process will be determined at various process operating conditions. All the data in this simulation process can be used to contribute to the development of technologies for CO_2 removal.

1.5 Organisation of this thesis

The structure of the thesis is outlined as follow:

Chapter 2 reviews open literature of current thesis and introduces researches which have been conducted in this regard. There are some brief explanations on amine based absorption process for carbon dioxide and reactivity of alkanolamines. The interaction involved during the simulations and the thermodynamic properties used in this study are also clearly explained in this chapter.

Chapter 3 concerns the methodology used in this study. The procedure and forcefields involve in the simulation process. This chapter also explains the method to interpret radical distribution function into graphical form to analyse the interaction between atoms.

Chapter 4 discuss the results obtain from research and simulation carried out. The results will be related with the amine based absorption to give insight on how the interaction occur during the simulation and determine the optimum temperature of the absorption process.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Introduction

This chapter discusses carbon dioxide separation technologies, amine based absorption process, molecular dynamic simulation (MD) and modelling of molecules. The aim of this chapter is to review the fundamental science of the absorption process and the simulation technique.

2.2 Carbon dioxide separation technologies

Nowadays, there are many technologies available for gas separation especially CO_2 capture system. The known technologies are adsorption, membrane separation, cryogenic separation, physical and chemical absorption. The choice of a suitable technology depends upon the characteristics of the gas stream from which the CO_2 needs to be separated, the sensitivity of the method to other impurities or trace components, the amount of CO_2 recovery, the capital and operating costs and the environmental impacts (waste or by-product production) (Steeneveldt et al., 2006).

a) Adsorption

This technology is used for carbon dioxide removal from the flue gas using solid adsorbents. These solid adsorbents have a high surface area and desorb through a regeneration process. The adsorption process is typically cycled between two beds of adsorbents; one bed is adsorbing CO_2 while the other is being regenerated. In the regeneration process, CO_2 can be desorbed by either pressure swing adsorption (PSA) (pressure reduction) (Yokoyama, 2003), temperature swing adsorption (TSA) (temperature increase) (Drage et al., 2009), electrical swing adsorption (ESA) (Grande et al., 2009), which adjusts the electric current passed through the adsorbents, or vacuum swing adsorption (VSA) (Chaffee et al., 2007). PSA is commercially used for gas separation, in hydrogen production and in the removal of CO_2 from natural gas (Yong et al., 2002). However, the key challenge of CO_2 capture using adsorption technology is low capacity and selectivity for current adsorbents, which limits its application for large scale CO_2 removal.

b) Membrane separation

Application of membrane separation typically involves the use of polymer-based membranes employing permeation process. Form of membrane treatment includes spiral-wound system, tubular systems and hollow fiber. However, membrane is determined as not effective method because it cannot achieve high degrees of separation. It needs to have multiple stages and/or recycle of one of the streams is required. This will lead to increased energy consumption, cost and complexity. The advantages of a gas membrane separation process include lower capital cost, ease of skid-mounted installation, lower energy consumption, its ability to be installed in remote areas, especially offshore, and flexibility (IPCC, 2005).

The phenomenon of membrane separation occurs in 4 steps:

- Adsorption of the CO_2 by the active surface of the membrane (at the raw gas pressure)
- Dissolution of the CO_2 in the membrane
- Diffusion of the CO_2 through the membrane
- Desorption of the CO_2 from the membrane (at low pressure)

The adsorption of the CO_2 is better at high pressure (high CO_2 partial pressure). The process is then not well suited to low pressure operations. The polymeric material to be selected for membrane construction must be permeable to CO_2 but also selective (to avoid permeation of hydrocarbon gas components).

c) Cryogenic separation

The cryogenic separation is a process for the removal of CO_2 from natural gas. The process originally developed by KOCH Process Systems Inc. was titled "RYAN/HOLMES Process" after two employee-inventor and involves the use of a hydrocarbon additive usually present in the natural gas to provide a particular benefit to the distillation (lowering the CO_2 freezing point). The "RYAN/HOLMES Process" uses Natural Gas Liquid (NGL) which is extracted from the feed stream itself. (Maddox, 1982)

The principle of the "RYAN/HOLMES Process":

- Separation of methane from CO_2. This separation uses the NGL stream to avoid CO_2 freezing and takes place in the "RYAN/HOLMES demethanizer".

- Separation of CO_2 from ethane plus (C^{2+}). This separation uses the NGL stream to break the CO_2/ethane azeotrope.

Since this separation requires low temperature, its best utilization is the LNG manufacture. Derived cryogenic processes working at temperature above the CO_2 solidification point have been implemented for the bulk removal of CO_2 from natural gas.

d) Physical absorption

Physical absorption relates to the use of molecular sieves for the removal of acid gases. It uses organic or inorganic solvents to physically absorb the CO_2. This process is mostly applicable to gas streams which have relatively concentrated streams of CO_2 at high pressure. They are commercially used to remove acid gases, CO_2 and H_2S from natural gas for removing CO_2 from synthesis gas in ammonia, hydrogen, and methanol production. Some commercially available solvents include dimethyl ether, propylene carbonate, N-methyl-2-Pyrrolidone and methanol (Abass, 2010). For the process of physical adsorption, firstly the untreated gas is contacted with the solvent which absorbs CO_2 in an absorber column. Secondly, the CO_2 rich liquid stream exits the bottom of the absorber and then passes through a series of flash drums at varying pressures. Finally, depressurization will release the CO_2 from the solvent and the lean solvent is then recycled back to the absorber. The energy consumption for physical absorption is low as only the energy for pressurizing the solvent (light pumping) is required. The physical absorption is not economically competitive for low partial pressure of CO_2 because the capacity of physical solvents is strongly dependent on partial pressure (Kohl & Nielsen, 1997).

e) Chemical absorption

Chemical absorption process is based on a contact between the gas to be treated (feed gas) and an aqueous solution containing one of the above solvents. Acid gas in the feed gas is a weak acid which reacts with the alkanolamine or alkaline salt to give bisulfide (with H_2S) and bicarbonate (CO_2). In the chemical absorption, the CO_2 is absorbed and chemically react with the solvent. The chemical absorption takes place in a fractional column which is equipped with trays or packing. The gas enters the column at the bottom tray. The aqueous solution enters the column at the top tray. There is a heat of reaction between the solvent and the acid gas during the absorption, which is exothermic. The

treated gas water content will be higher than the feed gas water content since the treated gas exits the unit at a higher temperature than the feed gas. Chemical absorption processes are applicable for removing dilute concentration of CO_2 at low partial pressure. However, the challenge of this technology for CO_2 capture from power plant is due to high energy demand for solvent regeneration and solvent degradation. The solvent such as amine solution, aqueous ammonia and carbonate removers CO_2 from the gas stream by means of chemical reactions in the absorption column. The ideal chemical solvent should have the following characteristics (Davidson, 2007):

- Lower energy/cost for solvent regeneration
- Higher absorption rate
- Higher reactivity for CO_2 capture
- Better stability, less degradation and lower corrosivity
- Lower solvent cost
- Lower environmental impact

2.3 Amine based absorption process

2.3.1 Process

As mention in section 2.2, there are techniques available to remove CO_2 from gases mixture. Chemical absorption technology, amine based absorption is most effective for CO_2 removal from flue gas (Chakrawarti & Hunek et al., 2001). The reaction between CO_2 and amines will enhance the driving force for the separation even at low partial pressure of CO_2. The cost of this technology is most cost-effective by gaining high purity (<99%) CO_2 vapor from flue gases in a single step.

Figure 2-1 shows a simplified process flow diagram for chemical solvent-based acid gas treating. Cooled synthesis gas enters the bottom of an absorber where it contacts an amine solution. The treated gas exits at the top of absorber. Lean solution enters the top of the absorber and counter-currently contacts the synthesis gas using trays or packing, absorbing acid gas contaminants as it passes down the column. Warm rich solution leaves the bottom of the absorber and is routed to a regenerator. Steam stripping is used to remove acid gas from the solution. The hot lean solution is then cooled prior to returning to the absorber. A lean/rich cross exchanger is used to reduce the sensible heat load on the regenerator reboiler (Echt, 1997).

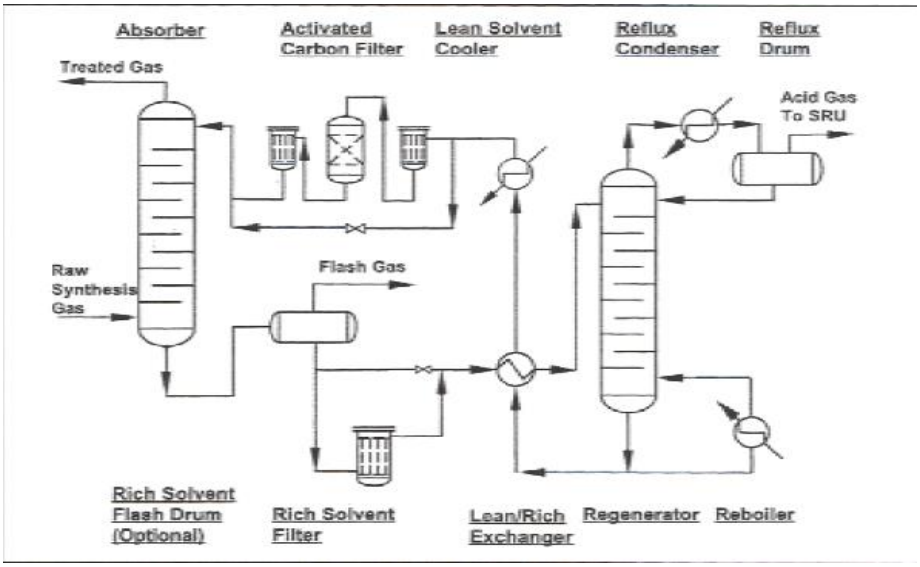

Figure 2-1: Process flow diagram of amine absorption process (Echt, 1997)

2.3.2 Categorization of Alkanolamines

According to Farmahini (2010), alkanolamines are a group of ammonia derivatives consisting at least one hydroxyl group and one amine group. Based on the number of substituents on the nitrogen atom, there are different subcategories for the amine group. Considering this general definition, it is normal to distinguish between the following classes of alkanolamines:

1. Primary alkanolamines: In this group of alkanolamines, nitrogen atom carries one substituent group (ethanol group) and two hydrogen atoms which are directly bonded to the nitrogen. MEA (monoethanolamine) is an example for this subcategory.

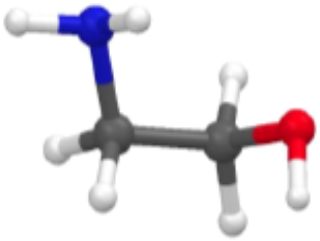

Figure 2-2: Molecular structure of monoethanolamine, C_2H_7NO

2. Secondary alkanolamines: In this subcategory, nitrogen atom is bonded to two ethanol group and one hydrogen atom. The best example is DEA (diethanolamine).

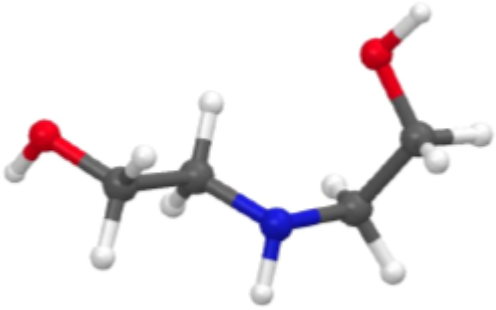

Figure 2-3: Molecular structure of diethanolamine, $C_4H_{11}NO_2$

3. Tertiary alkanolamines: The nitrogen atom of this alkanolamine is not bonded to any hydrogen atom but bonded to the alkyl or alkanol groups. MDEA (methyldiethanolamine) is an example for this subcategory.

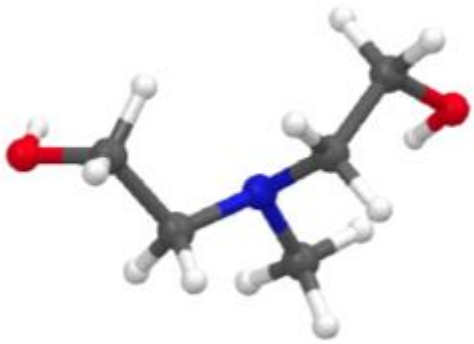

Figure 2-4: Molecular structure of methyldiethanolamine, $CH_3N(C_2H_4OH)_2$

In this simulation study, the alkanolamine used is methyldiethanolamine (MDEA). MDEA is an alkyl alkanolamine with colorless to yellow liquid tertiary amine compound. It is made up of 5 carbon atoms, 2 oxygen atoms, 13 hydrogen atoms and 1 nitrogen atoms. 2 ethanol molecules and 1 methane molecule are bonded to the nitrogen atom. It has an ammonia-like odor. It can undergo the typical reaction of amines and alcohols to form quaternary amine salts, soaps, and esters since it combines both characteristics. MDEA is considered slightly toxic MDEA is always used as an intermediate in the synthesis of numerous products such as coatings, polishes, textile lubricants, detergents, pesticides, personal products and pharmaceuticals (Dow, 2014).

In absorption process, the alkanolamines and their aqueous solutions will absorb carbon dioxide at lower temperatures and release the acid gases at higher temperatures.

This forms the basis for processes which separate carbon dioxide from gas streams. Normally, MDEA is used in tail gas treating for the removal of carbon dioxide. These units will, in most cases, permit 60 to 80% of the carbon dioxide to remain in the treated gas stream. MDEA is also used in natural gas plants for the bulk removal of carbon dioxide while producing a gas stream containing 0.25 grains hydrogen sulfide/100 scf. Bulk carbon dioxide removal can be realized with methyldiethanolamine when the CO_2:H_2S ratio ranges from 100 to 1,000 (Laffans Petrochemical, 2007).

2.3.3 Reaction between Amines and CO_2

Amine based absorption process technology is used to capture CO_2 in a large scale with amines as the solvent. There are three main type of amines can be used in absorption process. The three main types are primary amines (MEA), secondary amines (DEA) and tertiary amines (MDEA) (Nathalic et al., 2012).

The reaction between primary and secondary amines with CO_2 will form carbamate ion. Where else tertiary amines will form bicarbamate when react with CO_2. The reactions during the absorption process can be expressed as the equations below (Donaldson & Nguyen, 1980):

Primary or Secondary amines,

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+ + R_1R_2NCOO^- \ (carbamate) \qquad \text{Equation 2-1}$$

Tertiary amines,

$$R_1R_2NH + H_2O + CO_2 \leftrightarrow R_1R_2NH^+ + HCO_3^- \ (bicarbamate) \qquad \text{Equation 2-2}$$

Interest of using MDEA which is a tertiary amine increased significantly in the last decade. The main advantages of MDEA instead of more traditionally used primary and secondary amines are its relatively high capacity, a low vapor pressure and small enthalpy of reaction with acid gases. Since the CO_2 reaction rate with MDEA is slow, the addition of small amounts of fast reacting amines is necessary to apply this process in flue gas treatment (Kierzkowska-Pawlak & Chacuk, 2010).

2.4 Molecular dynamic simulations

Molecular dynamics (MD) simulation is routinely used as a tool to investigate structure, dynamics and thermodynamics of materials and biological systems. It can be classified as a computer experiment which can provide average prediction results for a new theory or process (Frenkel et al., 2002). This computational technique originally started as the need to incorporate physical theory (electron and nuclei) to explain the details in chemistry (Berendsen et al., 1987). As Schlecht (1998) said in the preface of his book; ―Computer-aided molecular modelling doesn't exist for its own sake, but to contribute to scientific endeavour, and enable the scientist to work smarter. Therefore the computer simulation is a new emerging tool where the scientist has to consider due to its ability to produce molecular level information for scientists.

Molecular dynamic simulation is a numerical method of statistical molecular mechanics which has been developed to integrate Newton's second law by B.J Alder and T.E Wainwright in the 1950s. This integration simulates the dynamic environment of molecules by calculating each particle position and force acting on it during simulation. The law is expressed by Equation 2-3.

$$f_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} \qquad \text{Equation 2-3}$$

The mass of the particle represents m_i, a_i is acceleration and f_i is the force acting on the particle which can also be calculated using the Equation 2-4 where the $V(r_i)$ is the potential energy with respect to the position of the particle.

$$f_i = \nabla_i V(r_i) \qquad \text{Equation 2-4}$$

Simulation integrates the Newton equation of motion for each atom in the system with the structural constraints and molecular interactions such as intermolecular and intramolecular interaction (Allen & Tildesley, 1987). The intermolecular interaction is one of the forces incorporated which plays a significant role towards the system as well as process. Forces data will then be used to solve the velocity of atoms.

MD simulation will generate the trajectory in phase space which can be used to calculate macroscopic properties, structural properties and transport properties (Berendsen et al., 1987). Examples of macroscopic properties of the system are kinetic and potential energy, density, and pressure. While the structural property such as radial

distribution function can be used to describe the intermolecular interaction in the system. This interaction will then affect transport properties such as the diffusion coefficient. Nevertheless there are some limitations which are accuracy of the force field, simulation time and size of the system in the molecular dynamics simulation technique to produce acceptable results (Berendsen et al., 1987).

Simulation time that is too short may not be enough for the system to equilibrate and produce reliable results. A large system may require expensive calculation with adverse boundary effects and a system that is too small may not represent the real process with insufficient statistical accuracy (Berendsen et al., 1987). Therefore these factors should be taken into account before the simulation process begins.

2.4.1 Molecular Dynamic Time Integration Algorithm

A number of time integration algorithms have been developed to integrate the equation of motion. The time integration algorithm is a numerical method which is the engine of the MD program and it is based on the finite difference methods (Gunaratne, 2006). The time integration algorithm iterates the equations for *t* time and at a later time (t + Êt) and then produced a trajectory of the time evolution. There are a few common time integration algorithms such as the Verlet, Velocity Verlet and Leap-Frog algorithm.

The velocity of the Verlet algorithm solves the Verlet algorithm deficiency to calculate the velocity explicitly (Jang, 2007) which may affect the simulation with constant pressure. The velocity of Verlet requires a modest operation mode and storage, and allow the usage of a relatively long time steps duration as the position (*r),* velocities (*v*) and acceleration (*a*) are calculated at the same time with high precision (Rai, 2012) using Equation 2-5, 2-6 and 2-7. This factor has attracted most MD simulation software developers to use this algorithm beside its capability to conserve the energy with numerically stable and time reversible properties.

$$a(t+\delta t) = \frac{f(t+\delta t)}{m} \qquad \text{Equation 2-5}$$

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 \qquad \text{Equation 2-6}$$

$$v(t+\delta t) = v(t) + \frac{1}{2}[a(t) + a(r+\delta t)]\delta t \qquad \text{Equation 2-7}$$

There are some criteria for a good algorithm to integrate Newton's equations of motion:

1. Speed is not important since most of the time is spent on calculating non-bonded interactions and forces rather than integrating the equations of motion. For Verlet algorithm, it is fast but relatively unimportant for calculations.
2. Accuracy for large time steps is important because the longer the time step, the fewer evaluations of the energies and forces are needed. Verlet algorithm is not very accurate for long time steps since it requires only short time steps (Δt= 1fs) for simulations.
3. Energy conservation is an important criterion where one has to distinguish between short-time and long-time energy conservation. In general, one comes to the cost of the other. For Verlet algorithm, the short-term energy conservation is fair and, more important, it exhibits little long-term energy drift.
4. Newton's equations of motion are time reversible, and so should be the integration algorithms. Non-reversible algorithms will have serious long-term energy drift problems. For Verlet algorithm, time reversible is related to its little long-term energy drift.

There are several algorithms that are equivalent to the Verlet scheme. Leap Frog algorithm evaluates the velocities at half-integer time steps and uses the velocities to compute the new positions (Hinchliffe, 2008).

$$v\left(t-\frac{\Delta t}{2}\right)=\frac{r(t)-r(t-\Delta t)}{\Delta t} \qquad \text{Equation 2-8}$$

Here $v(t+\frac{\Delta t}{2})$ can be approximated via a Taylor series expansion so that $r(t+\Delta t)$ follows:

$$v\left(t+\frac{\Delta t}{2}\right)=v\left(t-\frac{\Delta t}{2}\right)+\Delta t\frac{f(t)}{m} \qquad \text{Equation 2-9}$$

$$r(t+\Delta t)=r(t)+\Delta t v(t+\frac{\Delta t}{2}) \qquad \text{Equation 2-10}$$

The Leap Frog algorithm give rise to the same trajectories as the Verlet algorithm since it is derived from the latter. Since the velocities and positions are not defined at the same time, the kinetic and potential energy are also not defined at the same time since we cannot directly compute the total energy in the Leap Frog scheme.

Velocity Verlet algorithm is similar to the Leap Frog algorithm but the velocity and position are calculated at the same time:

$$r(t+\Delta t) = r(t) + \Delta t v(t+\Delta t) + \frac{f(t)}{2m}\Delta t^2 \qquad \text{Equation 2-11}$$

$$v(t+\Delta\, t/2) = v(t) + \frac{f(t)}{2m}\Delta t \qquad \text{Equation 2-12}$$

$$v(t+\Delta\, t/2) = v(t+\Delta t) - \frac{f(t+\Delta t)}{2m}\Delta t \qquad \text{Equation 2-13}$$

$$v(t+\Delta t) = v(t) + \frac{f(t+\Delta t)+f(t)}{2m}\Delta t \qquad \text{Equation 2-14}$$

The new velocities can only be computed once $r(t+\Delta t)$, thus the forces $f(t+\Delta t)$ have been computed. It can be shown that the Velocity Verlet algorithm is equivalent to the basic Verlet algorithm.

For most MD applications, Verlet-like algorithms are perfectly adequate. Higher-order algorithms (i.e, algorithms that employ information about higher-order derivatives of the particles coordinates) allow to use longer time steps without loss of short-term accuracy. However, higher-order algorithms require more storage and the calculation of the computation of higher-order terms may be time intensive too. Moreover, higher-order algorithms are not time reversible, for example the so-called predictor-corrector algorithms, which are the most popular class of higher-order algorithms used in MD simulations.

2.4.2 Periodic boundary condition (PBC)

The MD simulation normally runs in a confined and finite system or boundary system. There are few types of boundary condition which can be implemented in the MD simulation such as vacuum boundary condition and periodic boundary condition. The vacuum boundary condition is the simplest choice that simulates the system at zero pressure as gas phase. In the simulations, it is not suitable for molecules with distorted shape (Gunsteren et al., 2001). Periodic boundary condition is the most popular choice of boundary conditions. These boundary conditions are used to simulate processes in a small part of a large system as shown in Figure 2-5.